VII.15 Dense Membranes for Anode-Supported All-Perovskite IT-SOFC

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Objectives

- Synthesize fine, homogeneous, phase-pure perovskites in the form of bulk (powders) and thin films to be used as components for developing zero-emission solid oxide fuel cells (SOFCs) capable of operating at reduced temperatures (˜800°C).
- Study the effect of composition on the microstructure (grain size, grain boundaries, surface texture), magnitude of oxygen permeation, O_2 exchange rates and long-term stability.
- Measure the AC impedance at higher temperatures and investigate the effect of electrical conductivity on the electronic structure using x-ray absorption near edge spectroscopy (XANES) and extended x-ray absorption fine structure spectroscopy (EXAFS).
- Assemble all-perovskite SOFCs made from dense ceramic electrolyte membranes (LSGM: $La_{0.8}Sr_{0.2}Ga_{0.875}Mg_{0.125}O_{3-x}$) sandwiched between porous electrodes (based on Ni as anode and electronically conducting $LaNi_{0.6}Fe_{0.4}O_3$ and/or $La_{0.8}Sr_{0.23}CoO_3$ ceramic cathode).
- Evaluate the cost, performance, power generation capabilities, and emissions of the above SOFCs while optimizing the reduced-dimensionality structures needed to demonstrate a zero-emission unit by the end of the three-year period.
- Create an interest among African American undergraduate and graduate students to develop theses related to the development of all-perovskite anode-supported intermediate-temperature SOFCs (IT-SOFCs).

Introduction

To make solid oxide fuel cells (SOFCs) commercially viable for environment-friendly energy generation, it is of considerable interest to develop new techniques for large-scale, cost-effective preparation of perovskite-based multicomponent materials for application as cathode, anode and electrolyte. Preparation of perovskites using conventional solid-state sintering powder preparation routes is inconvenient when the requirement is for a fine, homogeneous, and phase-pure powder. Conventional processes have limitations due to the high temperature and prolonged period of heating involved, as highlighted by the following examples:

- Solid-state synthesis of $LaCrO_3$ often leads to volatilization of CrO_3.
- Cathode materials need to be porous for easy diffusion of O_2 to the electrode-electrolyte interface, but conventional solid-state technique does not result in porous materials.
- Formation of undesirable phases like $La_4Ni_3O_{10}$ in the synthesis of $LaNi_{1-x}Fe_xO_3$ can result in mismatch of thermal expansion coefficients.

Approach

For efficient performance of the $LaCrO_3$ interconnector, its sintered density should be close to its theoretical density (within =96%) or the porosity should be negligible to avoid interdiffusion of H_2 and O_2. High sintered density is usually achieved by high-temperature treatment (=1200°C) for prolonged duration. But in the case of $LaCrO_3$, large-scale synthesis of the pure phase is challenging because

loss of CrO_3 occurs during extreme conditions prevalent during conventional solid-state synthesis routes normally employed in industry. Fast synthetic techniques can prevent the loss of CrO_3. The microwave-assisted route is a quick and efficient method for synthesis and sintering of materials. Recently, K.J. Rao et. al. reported synthesis of monophasic $LaCrO_3$ in a short time by microwave irradiation of a heterogeneous mixture of La_2O_3 and Cr_2O_3 embedded in graphite. The synthesis is fast because both graphite and Cr_2O_3 are good microwave susceptors. Although their results are interesting, it was felt that the porosity in $LaCrO_3$ prepared by microwave route can be further decreased. Porosity depends on the microstructure, which in turn is influenced to a great extent by the precursor chemistry and the synthetic conditions. Our approach to the minimization of porosity is to explore a combination of sol-gel and microwave techniques. The results from this investigation will clarify the following:

(1) Whether or not there is any advantage of starting with a homogeneous mixture of La_2O_3 and Cr_2O_3 instead of a heterogeneous mixture as reported earlier. The homogeneous amorphous mixture is being generated using Pechini-type sol-gel route.

(2) The correlation between the morphology of the precursor mixture obtained from the sol-gel route and the porosity of the final product after irradiating with microwaves. Systematic variation of the sol-gel parameters like nature of the ligand, metal-ligand ratio, thermal treatment etc. is being carried out to generate different morphologies of the precursor mixture.

(3) The effect of duration of microwave irradiation on porosity.

Unlike interconnectors, cathodes for SOFC application need to be highly porous to facilitate oxygen diffusion to the electrode-electrolyte interface. One of the problems associated with cathodes is that they tend to lose their porosity at high fuel cell operating temperatures. This phenomenon is related to the microstructure. It has been shown that desired microstructures can be obtained by employing synthetic techniques such as hydro/solvo-thermal and template-based routes.

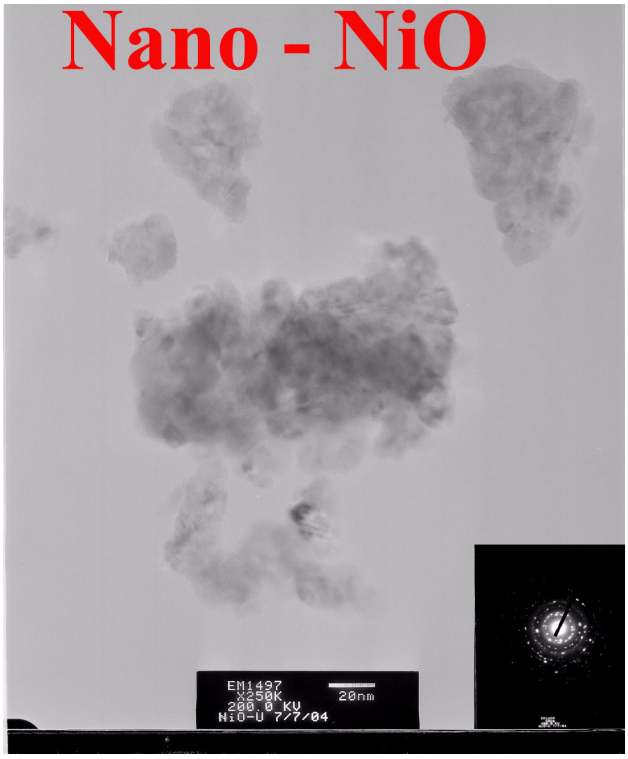

Figure 1. HRTEM Micrograph of Nanocrystalline NiO

In such synthetic routes, yield is very low and not suitable for large-scale synthesis. Hence there is a need for a synthetic technique which results in material where porosity is retained and can be prepared at a large scale. We are approaching this issue by adopting a combination of the Pechini-based method and scalable microwave processing.

Results and Discussion

We are employing a microwave-assisted solution combustion, mechano-assisted (ball milling), and pulsed laser deposition techniques to fabricate **dense** ceramic **membranes** on porous crystalline substrates. We have developed a combustion synthesis method using inexpensive, safe, water-soluble dimethyl urea (DMU), which is ignited at a temperature much lower than the actual phase-formation temperature. This fuel is new and has not been reported earlier. We have demonstrated the utility of this fuel and successfully prepared nanocrystalline NiO. The particle size of the NiO is ~ 50 nm, as determined by high-resolution transmission electron microscopy (HRTEM), shown in Figure 1.

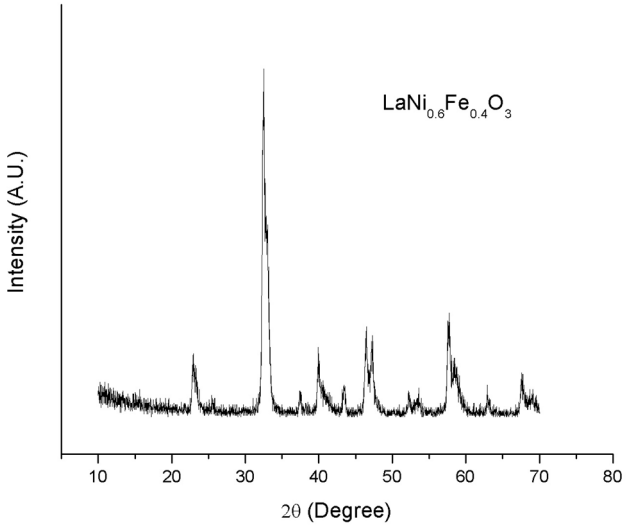

Figure 2. XRD Plot of $LaNi_{0.6}Fe_{0.4}O_3$ Powder Sample

The utility of this fuel further was extended to synthesize sub-micron sized mixed-perovskite-based oxides to be used in the fabrication of SOFCs. The properties of the SOFC components synthesized with DMU will be compared with those obtained by using other common fuels like glycine, citric acid, etc.

$LaNi_{1-x}Fe_xO_3$ was synthesized using the novel fuel developed in our laboratory. Figure 2 shows the x-ray diffraction (XRD) plots of the powder sample. The crystal structure was rhombohedral, and there were some impurities seen in the XRD. HRTEM, shown in Figure 3, reveals that the particle size is ˜100 nm. We are now optimizing the synthesis procedure to further reduce the particle size and to get single phase at 800°C.

We have also successfully prepared these materials in a very short time (10-15 minutes) by subjecting sol-gel generated amorphous precursors to microwaves of 2.45 GHz in a multimode microwave oven coupled with suitable microwave susceptors. The cathode (that is the electrode at the air side of the fuel cell) has to reduce the oxygen molecules (O_2) of the air to oxygen ions (O^{2-}), which then migrate to (and through) the electrolyte. The cathode must have a porous structure to enable gas transport to the cathode's surface.

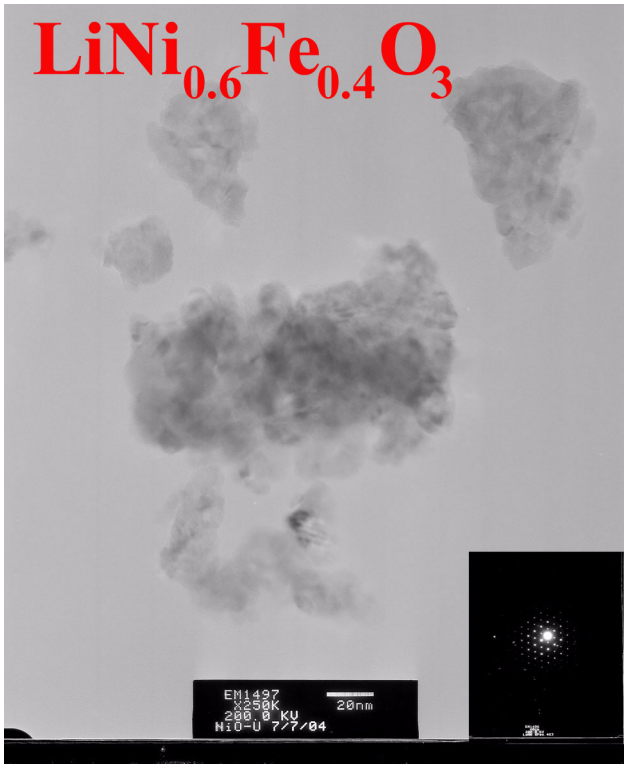

Figure 3. HRTEM Micrograph of $LaNi_{0.6}Fe_{0.4}O_3$

We have successfully prepared $LaCrO_3$ to be used as an interconnect in a very short time (10-15 minutes) by subjecting sol-gel generated amorphous precursors to microwaves of 2.45 GHz in a multimode microwave oven coupled with suitable microwave susceptors. No apparent loss of CrO_3 has been observed for $LaCrO_3$. Products have been characterized by XRD and scanning electron microscopy. Conductivity measurements are in progress. The products are largely monophasic and stoichiometric. The oxide particles are of submicron size. $LaCrO_3$ has been microwave sintered to a remarkably high crack-free density of 96% in 10 minutes.

We are trying to evaluate valency of each transition metal in these perovskites using XANES, and to explore the relation between electrical conductivity and changes in electronic structure.

Summary

1. Combustion and mechano-chemical (ball milling) synthesis experimental stations were acquired and installed.

2. Research microwave system for high-temperature (1700°C) synthesis was acquired and installed.

3. Promising perovskite cathode, electrolyte, and interconnect were identified and synthesized.

4. The electrochemical impedance spectroscopy, EXAFS, XANES, and diletaletry measurements and fabrication development are in progress.

Future Plans

1. Once the synthetic parameters are optimized for $LaCrO_3$ and $LaNi_{0.6}Fe_{0.4}O_3$, the electrical conductivities of the samples will be measured.

2. Attempt synthesis of lanthanum strontium magnesium gallate (LSGM) electrolyte by regenerative sol-gel synthesis and carry out impedance measurements.

3. Attempt deposition of thin layer of LSGM electrolyte on $LaNi_{0.6}Fe_{0.4}O_3$ cathode.

4. We plan to carry out electrophoretic deposition of the dense LSGM samples on $LaNi_{1-x}Fe_xO_3$ porous cathodes presently being developed in our laboratory. To realize thin, dense O_2-semipermeable membranes on single crystalline substrates, we are preparing thin films using pulsed laser deposition (PLD). The technique of PLD seems very well suited to deposit prototype thin perovskite films with various compositions.